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Abstract

The Groningen AMS target laboratory has a capacity of producing 2000 targets annually. Samples are combusted by a CN analyser/mass spectrometer combination. A 25-fold graphitization setup is employed. We emphasize a combination of automation and quality. Backgrounds of better than 45 ka are routinely achieved. Test measurements on contamination, backgrounds and fractionation are reported.

1. Introduction

As is the case with the Groningen conventional laboratory, the AMS laboratory handles about 1000 samples annually. The Groningen AMS system has now been operational for two years, during which time about 4000 targets were produced; half of these are standards, backgrounds and targets for various test programs, the other half were targets for "real samples". These samples consisted of water (DIC, Dissolved Inorganic Carbon) from ground water and the ocean, marine and fresh-water carbonates, atmospheric CO_2, organic deposits such as peat, soils and macrofossils, and the complete spectrum of archaeological datable materials such as wood, charcoal and fossil bone. In addition, many samples arrived in the laboratory in the form of breakseals (CO_2 sealed in glass containers) ready for graphitization. Furthermore, special target preparation systems are made for PhD projects such as ocean DOC (Dissolved Organic Carbon), Particulate/Dissolved Inorganic/Organic Carbon in sediments and pollen concentrates. On these special projects we report elsewhere at this conference [1,2]. For a description and performance of the Groningen AMS system we refer to [3]. A diagram indicating the different sample materials handled by the AMS-sample laboratory is shown in Fig. 1.

2. Sample treatment

Analogous to the conventional ^{14}C laboratory which also has a capacity of about 1000 samples per year, we realised a separate preparation laboratory. The organic samples are chemically pretreated to remove contamination, before they are combusted to CO_2. The form and the intensity of the pretreatment depends on the type, quality and quantity of the sample. The usual method is Acid-Alkali-Acid (AAA) for the peat and other organic deposits, charcoal and wood, Longin for bone and phosphoric acid for carbonates. For a complete description we refer to literature [4,5] with the obvious note that the amount of material for AMS is scaled down considerably.

For inorganic samples bi-carbonate from water is converted to CO_2. CO_2 from air samples is trapped cryogenically. Breakseals are broken on one of the laboratory's mass spectrometers, enabling direct measurements of stable isotopic ratios (^{13}C, ^{18}O); the samples then are trapped cryogenically and transferred to the graphitization setup.

The organic samples are combusted in an automatic CN-analyser, of which we employ two: Europa Scientific

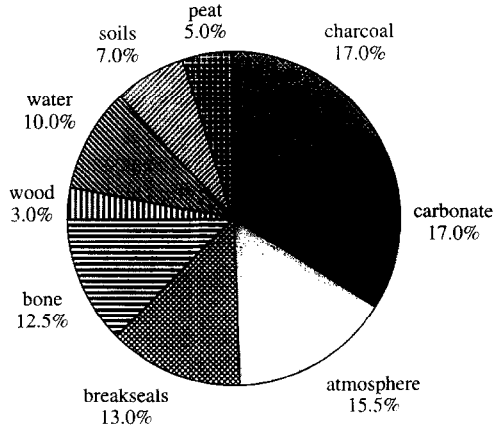

Fig. 1. Diagram indicating the various sample materials handled by the Groningen AMS laboratory in the first two years of operation. The total number of samples is about 2000.

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20/20-roboprep CN combination and Fisons/Carlo Erba Optima/NA 1500 combination. Both consist of a Cr_2O_3 flash combustion tube, Ag and CuO purification furnaces and a Cu reduction tube, a water trap and a gas chromatographic column to separate N_2 and CO_2. Each CN-analyser is coupled on-line to a stable isotope mass spectrometer enabling high-precision $^{13}\delta$ and $^{15}\delta$ determinations. The CO_2 is trapped cryogenically for graphitization later on. At present this is done manually; an automatic system is under construction.

3. Target production

The (purified) CO_2 as produced by the CN-analysers, breakseals, the water laboratory or the conventional ^{14}C laboratory (test measurements, standards and conventional samples which appear too small) is cryo-trapped in small glass vessels. These are transferred to the graphitization room. For graphite production, we employ the method of reduction under an excess of hydrogen gas, using iron powder as a catalyst [6]: $CO_2 + 2H_2 \rightarrow (Fe) \rightarrow H_2O + C$. Our excess of the H_2 gas is a factor of 2.5 times the amount of CO_2. The Fe-powder we use is < 325 mesh and $> 99.5\%$ pure. Before the actual reduction, we flush with H_2 in order to remove any unwanted CO_2. The CO_2 is transferred to a variable volume to adjust the amount of gas. The H_2O is trapped in a cold finger, which is cooled to -18°C by a Peltier element. The temperature of the reduction oven is kept at 600°C. During the reduction reaction, the pressure is monitored on computer screens. In general the reaction takes 200 min. We employ one 10-fold and one 15-fold graphitisation system, with volumes ranging from 3 to 8 ml. With this setup we can handle samples from 150 μg C and up.

The final step is transfer of the graphite powder to the target holder which fits in the caroussel of the AMS ion source. This is done in a laminar crossflow installation in a semi-clean room. The graphite is pressed into the target holder with a force of 2.5 Nm, either by hand (one by one) or by an automatic system. The automatic press is shown in Fig. 2. It consists of a wheel which can be loaded with 24 targets. First, the graphite powder is poured into the target through a funnel. Next, steel pins are loaded; the graphite is pressed from the back between these steel pins and a stainless steel foil, covering the front surface of the target. The force applied transfers the graphite powder to a solid with a flat and shiny surface (after removal of the foil); the force applied also joins the steel pin into the (aluminum) target holder.

The pressing force for the hand-press is applied by a torque-wrench; for the automatic system this is done with stepping motors; all loaded targets are pressed sequentially. The force applied on the target is measured by a pressure transducer in order to improve reproducibility of the pressing procedure; in the past we have experienced some difficulties with the hand-press in this respect.

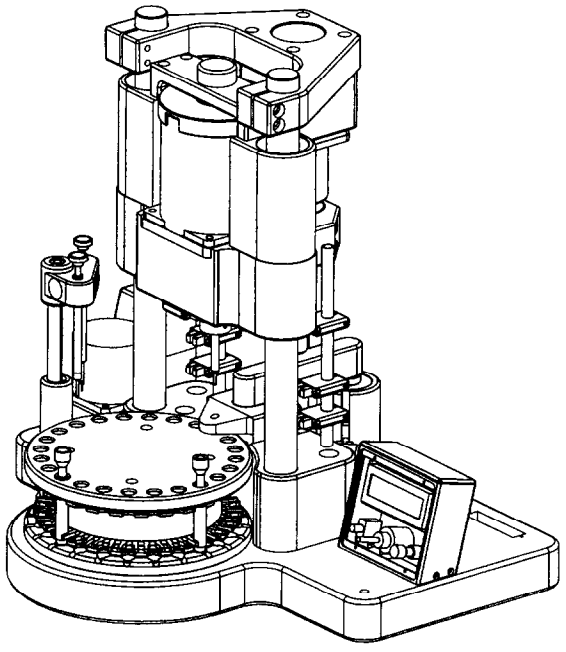

Fig. 2. The new automatic graphite target press.

We employ two types of targets. The standard ones have a 2 mm diameter graphite surface, and is sputtered at 8 positions during measurement [3]. For small samples (< 0.7 mg C), however, targets with a 1 mm diameter graphite surface are used. These small targets are also sputtered at 8 positions, albeit in a smaller radius. Both 1 and 2 mm targets can be pressed with the manual and automatic target press.

For logistic reasons, we assign a Groningen number (GrA) to each fabricated target, thus including standard, background and various test targets. Following the pressing procedure, the targets are stored in specially designed

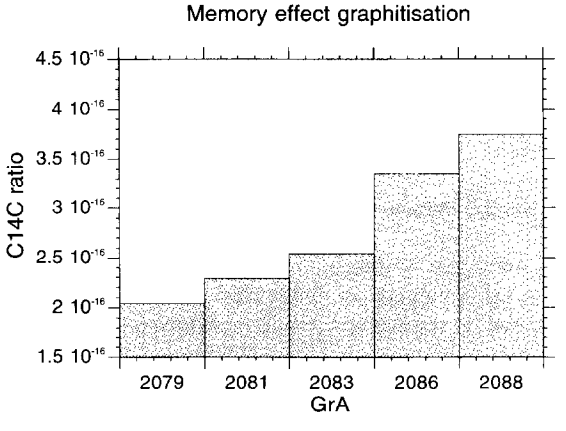

Fig. 3. Results from a memory-effect test of the graphite system: $^{14}C/C$ ratio (versus sample number) for anthracite. In-between each anthracite, a sucrose (IAEA-C6) sample was graphitised.

containers in a dry nitrogen atmosphere, until they are loaded in the ion source caroussel for measurement.

4. Experimental results

In the first two years of operation of the Groningen AMS system, the target laboratory has produced about 4000 graphite targets. For overall performance of the Groningen AMS we refer to [3]; for scientific results obtained thus far we refer to [2].

Here we report on specific tests concerning contamination effects in the laboratory, several background materials, the graphite system, and fractionation during graphite production.

Contamination has been tested by graphitising CO_2 from anthracite and sucrose in an alternating way. This "sandwich test" mimics the worst possible case. The results for the 5 anthracite samples are shown in Fig. 3, clearly indicating a small memory effect due to the sucrose. The memory effect is roughly a factor of 2 for this procedure. The sucrose measurements (performed inbetween the anthracites) are omitted in the figure.

Backgrounds of the target preparation laboratory have been investigated extensively. Various background materials and sample handling systems were tested, with the results shown in Fig. 4. The lowest background has been obtained from a graphite rod, which could be mounted in a target holder and was not exposed to any handling in the sample laboratory. The $^{14}C/C$ ratio (per gram of carbon)

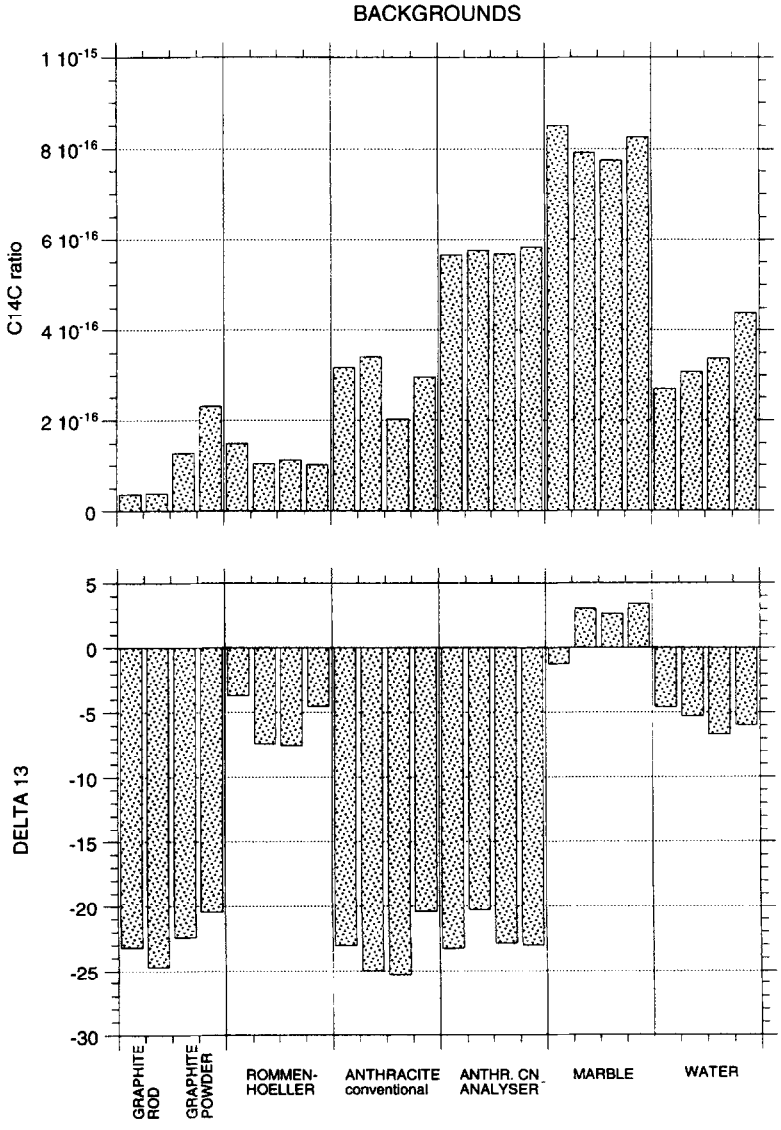

Fig. 4. Results for background measurements for materials indicated; ^{14}C (expressed in $^{14}C/C$ ratios), top and ^{13}C (in $^{13}\delta$), bottom.

for this background is 5×10^{-17}, corresponding to an age of about 65 ka. In addition, graphite powder was tested; the only sample handling was pressing in a target holder. In this case the background level is $1\text{–}2 \times 10^{-16}$. Rommenhöller is a fossil CO_2 gas which had to be graphitized and pressed; the background level is 10^{-16}. For anthracite we distinguish two batches. One is anthracite combusted by the conventional laboratory and used as background for the proportional gas counters; this high purity CO_2 is trapped and transferred to the graphitization setup. AMS measurement yields backgrounds of 3×10^{-16}. The second batch is anthracite, combusted by the CN-analyser as used for most organic AMS samples; this background anthracite is higher by a factor of 2 (6×10^{-16}).

Finally, we tested the backgrounds for two systems in use for CO_2 production from inorganic samples: marble and water, which was bubbled through with Rommenhöller-CO_2. These backgrounds were 8×10^{-16} and $3\text{–}4 \times 10^{-16}$, respectively. Representative background measurements are shown in Fig. 4; the top part of Fig. 4 shows the background in $^{14}C/C$ ratio, the bottom part shows the AMS-$^{13}\delta$ values for the same targets.

Fractionation during CO_2-graphite conversion has been studied in detail. In principle, fractionation is not critical for ^{14}C age determination, since the ^{14}C signal is fractionation-corrected. However, if one uses the mass spectrometer to determine the ^{13}C ratio of the CO_2 gas *prior* to graphitisation, the fractionation during the graphitisation process is *not* corrected for. A safer way is to use the ^{13}C measurement of the accelerator itself. Nevertheless, one would like to be able to rely on the $^{13}CO_2$ determination, so one gets an extra check parameter on the accelerator's performance: the $^{13}\delta$ comparison. We have repeated the graphitisation reaction several times with the same CO_2 under identical conditions. The main (reversible) reactions are: $CO_2 + H_2 \leftrightarrow H_2O + CO$ and $CO + H_2 \leftrightarrow H_2O + C$. Since the water vapour is continuously removed, the equilibrium of both reactions is almost completely on the right side of the reaction. In addition methane can be produced: $C + 2H_2 \leftrightarrow CH_4$; this is, however, an undesirable complication [7].

We analysed our graphitisation reactors in the following way: at a time varying between 1 and 100 min, the reaction is stopped. The rest gas mixture, consisting of H_2, CO_2, CO and possibly CH_4 is then transferred to a circulation system that separates the gases in the following way: all CO_2 is captured in a liquid air cold trap by circulating during ≈ 10 min, until there is no more pressure change. Then, the trap is isolated, and the rest gas is directed through a hot CuO oven ($T = 400$°C). This oven oxidizes CO (and H_2), but not (much of) the CH_4. The formed H_2O and CO_2 are trapped in a dry ice and liquid air trap, respectively.

The two "sorts" of CO_2, the original one, and the one oxidized from CO, are isotopically analysed on the SIRA-9 IRMS (as far as the amounts allow). Also the formed graphite is combusted and ^{13}C-analysed. Some of the graphite, however, is ^{14}C-analysed in the AMS. Also, all amounts of gas are measured. The isotope measurements are shown in Fig. 5, plotted as a function of the relative amount of CO_2 left at any time. The $^{13}\delta$ of the CO_2 and C, as well as the $^{14}\delta$ of C can be fitted with Rayleigh curves:

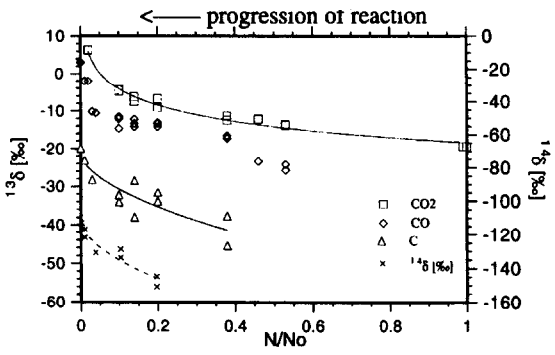

Fig. 5. Isotope ratios for CO_2, CO and C, plotted as a function of the amount of CO_2 left. The lines are fits of a simple Rayleigh function, for CO_2 and C. Also $^{14}\delta$ has been measured.

$$\delta = (N/N_0)^{\epsilon} + \delta_0 \quad \text{for the } ^{13}\delta \text{ of } CO_2, \quad \text{and}$$

$$\delta = (1 + \delta_0) \times \left(1 - (N/N_0)^{\epsilon - 1}\right)/(1 - N/N_0) - 1$$

for $^{13}\delta$ $^{14}\delta$ of C.

These fits yield the following fractionation factors for the reactions involved: $^{13}\epsilon = -6.6 \pm 0.2$‰ for $CO_2 + H_2 \rightarrow H_2O + CO$, and for $CO + H_2 \rightarrow H_2O + C$: $^{13}\epsilon = -39 \pm 3$‰ and $^{14}\epsilon = -81 \pm 14$‰. The fraction ratio $^{14}\epsilon / {}^{13}\epsilon$ of process 2 is 2.1 ± 0.4 which is according to what one would expect.

Finally, it appears that the ^{13}C value for the formed graphite is equal to the ^{13}C of the original CO_2 gas by better than 0.5‰. Still, further investigations are necessary, revealing directly the amount of CH_4. Clearly, this amount should be minimised.

5. Conclusions

In Groningen, we have setup an AMS sample handling system with a present capacity of 2000 samples annually, next to and partly intertwined with the conventional ^{14}C laboratory (1000 samples/year) and stable isotope facility (15000 samples/year).

We have achieved background levels for $^{14}C/C$ at best of 10^{-16}, depending on materials and setup used. In the near future, we will employ an automatic graphite target press (24 samples) and an automatic cryogenic trapping system, coupled to the CN analyser (combustion system). This device will operate fully automatic under processor control, greatly enhancing efficiency. An automatic carbonate system will be considered as well.

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